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NICKEL CARBONATE

[3333-67-3]

Formula: NiCO_3 ; MW 118.72

Two basic carbonates are known. They are $2\text{NiCO}_3 \cdot 3\text{Ni(OH)}_2 \cdot 4\text{H}_2\text{O}$ [29863-10-3], and $\text{NiCO}_3 \cdot 2\text{Ni(OH)}_2$ [12607-70-4], MW 304.17. The second form occurs in nature as a tetrahydrate, mineral, zaraitite. Commercial nickel carbonate is usually the basic salt, $2\text{NiCO}_3 \cdot 3\text{Ni(OH)}_2 \cdot 4\text{H}_2\text{O}$.

Uses

Nickel carbonate is used to prepare nickel catalysts and several specialty compounds of nickel. It also is used as a neutralizing agent in nickel plating solutions. Other applications are in coloring glass and in the manufacture of ceramic pigments.

Physical Properties

NiCO_3 : Light green rhombohedral crystals; decomposes on heating; practically insoluble in water, 93 mg/L at 25°C; dissolves in acids.

$2\text{NiCO}_3 \cdot 3\text{Ni(OH)}_2 \cdot 4\text{H}_2\text{O}$: Light green crystals or brown powder; decomposes on heating; insoluble in water; decomposes in hot water; soluble in acids and in ammonium salts solutions.

Zaraitite: Emerald green cubic crystals; density 2.6 g/cm³; insoluble in water; soluble in ammonia and dilute acids.

Thermochemical Properties



Preparation

Anhydrous nickel carbonate is produced as a precipitate when calcium carbonate is heated with a solution of nickel chloride in a sealed tube at 150°C. Alternatively, treating nickel powder with ammonia and carbon dioxide followed by boiling off ammonia yields pure carbonate.

When sodium carbonate is added to a solution of Ni(II) salts, basic nickel carbonate precipitates out in impure form.

Reactions

Nickel carbonate is the starting material for preparing many nickel salts. It reacts with dilute acids evolving carbon dioxide, and upon evaporation of the solution corresponding nickel salts are formed. The nitrate, sulfate and phosphate salts are prepared from carbonate. Similarly, reactions with hydrofluoric, hydrochloric, hydrobromic, or hydriodic acids yield hydrated nickel halides: namely $\text{NiF}_2 \cdot 4\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$, and $\text{NiI}_2 \cdot 6\text{H}_2\text{O}$, respectively:



Nickel carbonate decomposes to nickel oxide when strongly ignited:



Nickel carbonate, when dissolved in aqueous thiocyanic acid, yields a yellow brown precipitate of hydrated nickel thiocyanate:



Nickel carbonate forms many double salts, such as, $\text{Na}_2\text{CO}_3 \cdot \text{NiCO}_3 \cdot 10\text{H}_2\text{O}$ with alkali metal carbonates. However, such double carbonates usually are prepared by mixing an alkali metal or ammonium bicarbonate solution with a nickel salt solution, followed by crystallization.

Analysis

Anhydrous and basic nickel carbonates may be determined from x-ray diffraction measurements. The degree of hydration can be measured by DTA and TGA methods. Additionally nickel content in the carbonate may be determined by analyzing an acid solution of the salt using various instrumental methods (See Nickel).

NICKEL CHLORIDE

[7718-54-9]

Formula: NiCl_2 ; MW 129.60; forms a stable hexahydrate, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ [7791-20-0], MW 237.69 at ordinary temperatures.

Synonyms: nickel dichloride; nickel(II) chloride

Uses

Nickel chloride is used in nickel electroplating baths. It also is used to prepare various nickel salts and nickel catalysts; and in industrial gas masks to protect from ammonia.

Physical Properties

The anhydrous salt forms yellow crystal scales; deliquesces; density 3.55 g/cm³; melts at 1,001°C; sublimes at 973°C; highly soluble in water, 64 g/100mL at 20°C; soluble in alcohol.

The hexahydrate forms green monoclinic crystals; deliquesces; extremely soluble in water, 254 g/100mL at 20°C, and about 600 g/100 ml at 100°C; also very soluble in alcohol.

Thermochemical Properties

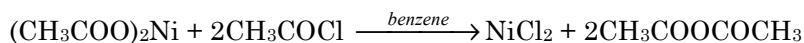
ΔH_f° (NiCl_2)	-72.98 kcal/mol
ΔH_f° ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	-502.67 kcal/mol
ΔG_f° (NiCl_2)	-61.92 kcal/mol

ΔG_f° ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	-409.54 kcal/mol
S° (NiCl_2)	23.34 cal/degree mol
S° ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	82.30 cal/degree mol
C_p (NiCl_2)	17.13 cal/degree mol

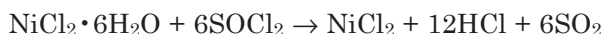
Preparation

Anhydrous nickel chloride is prepared by burning nickel in chlorine gas. Some other methods of preparation involve

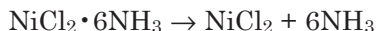
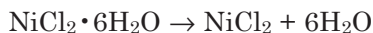
(1) the action of acetyl chloride on nickel acetate in a nonaqueous solvent such as benzene:



(2) the action of thionyl chloride on nickel chloride hexahydrate:



(3) heating nickel chloride hexahydrate or nickel chloride ammoniate:



The hexahydrate is prepared either by the action of hot dilute hydrochloric acid on nickel powder or by dissolving nickel oxide in dilute hydrochloric acid followed by crystallization. For the preparation of ammoniate, see Reactions below.

Reactions

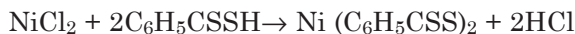
When ammonia gas is passed over anhydrous nickel chloride the product is an ammoniate, hexamine nickel chloride, $\text{NiCl}_2 \cdot 6\text{NH}_3$. Ammoniate also can be prepared in solution by dissolving nickel chloride hexahydrate in an aqueous solution of ammonia.

Nickel chloride forms double salts with alkali metal chlorides or ammonium chloride. Such double salts, $\text{NH}_4\text{Cl} \cdot \text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, are obtained as hexahydrate when crystallized from a mixed solution of nickel chloride and ammonium chloride in equimolar amounts..

Warming a solution of nickel chloride and sodium hydroxide at moderate concentrations may partially precipitate a basic salt of indefinite composition. The average composition of this salt is $\text{NiCl}_2 \cdot 3\text{Ni}(\text{OH})_2$. Salt composition may vary depending on reaction conditions.

When hydrogen sulfide is passed through a buffered solution of nickel chloride, nickel sulfide, NiS , precipitates.

An alcoholic solution of nickel chloride, when treated with an ethereal solution of dithiobenzoic acid, $\text{C}_6\text{H}_5\text{CSSH}$, blue nickel(II) dithiobenzoate, $(\text{C}_6\text{H}_5\text{CSS})_2\text{Ni}$, is formed:



The product oxidizes readily to a violet dimeric nickel(IV) complex.

Analysis

Elemental composition (for anhydrous NiCl_2): Ni 45.30%, Cl 54.70%

Percent composition of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$: Ni 24.69%, Cl 29.83%, H_2O 45.48%. Nickel may be analyzed in an aqueous solution of salt by various instrumental techniques (See Nickel). Chloride ion in the aqueous solution may be determined by titration with silver nitrate using potassium chromate indicator; or preferably by ion-chromatography. The solutions must be appropriately diluted for all analyses.

NICKEL COMPLEXES

Nickel forms a large number of complexes with various anions (monodentate, bidentate, and polydentate) and many neutral ligands. The most common coordination numbers of the metal in these complexes are six and four while the metal is usually in +2 oxidation state, Ni^{2+} . Also, some complexes of three and five coordinations exist. Several zero valent nickel complexes, such as nickel tetracarbonyl, and a number of substituted carbonyl complexes are well known.

The most common Ni^{2+} complexes of monodentate neutral ligands are octahedral ammine and aqua complexes $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, respectively, which form salts such as $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$, $[\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4](\text{NO}_3)_2$, $\text{Ni}(\text{NH}_3)_6\text{Br}_2$, and $\text{Ni}(\text{NH}_3)_6\text{SO}_4$. Such complex salts are stable at ordinary to moderate temperatures depending on size of the anion. The hexaaqua nickel ion is bright green while hexamine complex ion imparts blue to purple color to the solution.

Some other common ligands are pyridine (py), ethylenediamine (en), cyanide ion (CN^-), thiocyanate ion (SCN^-), acetylacetonate (acac), salicylaldehyde (sal), triphenylphosphine (PPh_3) and various trihalophosphines. Ethylenediamine and acetylacetonate are examples of two common bidentate ligands.

Nickel(0) complexes are obtained by substitution of CO molecules in nickel tetracarbonyl, $\text{Ni}(\text{CO})_4$. They contain ligands, such as CO, NO, PF_3 , PCl_3 and $\text{P}(\text{C}_6\text{H}_5)_3$ and their mixed combinations coordinated to nickel. Some examples of such zero valent complexes are $\text{Ni}(\text{PF}_3)_4$, $\text{Ni}(\text{PCl}_3)_4$, $\text{Ni}(\text{CH}_3\text{PCl}_4)_4$, $(\text{CO})\text{Ni}(\text{PF}_3)_3$, $(\text{CO})_3\text{Ni}(\text{PF}_3)$, and $(\text{PPh}_3)_2\text{Ni}(\text{NO})_2$.

A formal oxidation state of -1 for nickel also exists as, for example, in the nickel hydrocarbonyl, $\text{H}_2\text{Ni}_2(\text{CO})_6$.

Nickel(II) complexes of simple anions, such as F^- , Cl^- , SCN^- , NO_2^- , readily combine with alkali metal or ammonium ions forming their complex salts. For example, action of fluorine on a mixture of NiCl_2 and KCl yields diamagnetic

dipotassium hexafluoronickelate(IV), $K_2[NiF_6]$. Similarly, many complex nitrites of the type hexanitronickelates, $[Ni(NO_2)_6]^{4-}$ can be crystallized from solutions containing alkali and alkaline earth nitrites. An example is tetrapotassium hexanitronickelate(II), $K_4[Ni(NO_2)_6]$, a brownish red octahedral complex that can be crystallized from water. Similar cyanonickelate complex salts of alkali metals can be prepared by dissolving nickel cyanide in excess alkali cyanide solution followed by evaporation. An example of such four coordinated nickel(II) cyanide complex is yellow disodium tetracyanonickelate(II), $Na_2[Ni(CN)_4] \cdot 3H_2O$. A bridged binuclear nickel(I) cyano complex, potassium tetracyano- μ -dicyanonickelate(I), $K_4[(CN)_2Ni(CN)_2Ni(CN)_2]$ is an example of nickel's formal oxidation state being +1. Nickel forms both four and six coordinated thiocyanatonickelates with thiocyanate anions. Such complexes may be prepared by evaporation of solutions of nickel thiocyanate, $Ni(SCN)_2$ and alkali metal thiocyanates. They are usually recrystallized from alcohol and may be fairly stable in aqueous solutions without decomposition. Such complexes include green disodium tetrathiocyanatonickelate(II), $Na_2[Ni(SCN)_4] \cdot 8H_2O$ and the blue tetrapotassium hexathiocyanatonickelate(II), $K_4[Ni(SCN)_6] \cdot 4H_2O$.

The π -cyclopentadienyl nickel complex, $\pi-(C_5H_5)_2Ni$, known as nickelocene is analogous to similar sandwich complexes of iron and cobalt, ferrocene and cobalocene, respectively. This emerald-green paramagnetic complex, having a density of 1.47 g/cm^3 , melts at 173°C and oxidizes slowly in air. It is prepared by reacting sodium cyclopentadienide with nickel bromide dimethoxyethane. Many nickelocene derivatives have been prepared. They include green methylnickelocene; red cyclopentadienylnickel nitrosyl, $(\pi-C_5H_5)Ni(NO)$; the violet-red diamagnetic dimeric complex cyclopentadienylnickel carbonyl, $(\pi-C_5H_5NiCO)_2$ prepared by the action of nickelocene on nickel tetracarbonyl; the red complex bis(π -indenyl)nickel; and the greenish-brown tri-*n*-butylphosphine π -cyclopentadienyl methylnickel, $P(C_4H_9)_3(\pi-C_5H_5)NiCH_3$.

Many organonickel complexes of arene, aryl, allyl and other systems are known. They may be prepared by different methods from nickel tetracarbonyl or nickel halides using Grignard reagent or other organometallics. Arene-nickel complexes are made by the reaction of nickel bromide or nickel tetracarbonyl with aromatics. π -Allyl complexes of nickel, such as bis(π -allyl)nickel, $(\pi-C_3H_5)_2Ni$ can be made by the reaction of the Grignard reagent, allylmagnesium bromide, $CH_2=CH-CH_2MgBr$ with anhydrous nickel bromide. Alternatively, this compound or related complexes can be prepared by the reaction of allyl bromide, $CH_2=CH-CH_2Br$ with nickel tetracarbonyl. The violet nickel aryl complex bis(triphenylmethyl)nickel, $[(C_6H_5)_3C]_2Ni$ can be prepared by the reduction of nickel chloride in the presence of hexaphenylethane, $(C_6H_5)_3C-C(C_6H_5)_3$.

Several five-coordinate nickel(II) complexes having both the trigonal bipyramidal and square pyramidal geometry are known. Such complexes are of the type $[NiL_5]^{2+}$, $[NiL_3X_2]$ and $[NiL_4X]^+$, where L is a phosphine or arsine ligand and X is typically a halide ion but also can be a hydride or other anion. Such complexes in many cases contain unidentate ligands and their trigonal bipyramidal structure may change to square pyramidal geometry. Some typi-

cal examples of such nickel(II) five-coordinate complexes include $[\text{Ni}(\text{CN})_5]^{3-}$, $\text{NiCl}_2(\text{SbMe}_3)_3$, $[\text{NiMe}(\text{PMe}_3)_4]^+$, $[\text{NiBr}(\text{PMe}_3)_4]^+$, $[\text{Ni}(\text{SbMe}_3)_5]^{2+}$, and $[\text{Ni}(\text{Me}_3\text{AsO})_5]^{2+}$.

Four-coordinate nickel(II) complexes have both tetrahedral and square planar geometry. Square planar geometry that forms more stable complexes is preferred because the d^8 configuration of Ni^{2+} with eight electrons can occupy the four planar bonding orbitals more readily than the higher energy antibonding orbitals in tetrahedral coordination. The small number of tetrahedral complexes that are known are of the type $[\text{NiX}_4]^{2-}$, $[\text{NiX}_3\text{L}]^-$, and NiL_2X_2 , where X is a halide ion and L is a neutral ligand usually trialkyl arsine, AsR_3 ; triphenyl phosphine, PPh_3 ; or triphenyl phosphine oxide, O=PPh_3 . Some examples are $[\text{NiCl}_4]^{2-}$, $[\text{NiBr}_3(\text{OPh}_3)]^-$, and $\text{NiCl}_2(\text{AsMe}_3)_2$.

Most four-coordinate nickel(II) complexes are square planar. They are of red, brown and yellow color and practically all are diamagnetic. Some examples are red bis(dimethylglyoximate)nickel(II) and the yellow tetracyanonickelate(II) ion, $[\text{Ni}(\text{CN})_4]^{2-}$.

NICKEL CYANIDE

[557-19-7]

Formula: $\text{Ni}(\text{CN})_2$; MW 110.74; forms a stable tetrahydrate, $\text{Ni}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$ [13477-95-7], MW 182.79

Uses

Nickel cyanide is used for nickel plating. It also is used to synthesize butadiene from acetylene.

Physical Properties

The tetrahydrate, $\text{Ni}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$ constitutes apple green plates or powder; loses water of crystallization on heating at 200°C ; decomposes on further heating; insoluble in water; slightly soluble in dilute acids; soluble in potassium cyanide solution and in ammonia, caustic soda, caustic potash and other bases.

Preparation

Nickel cyanide is prepared by treating a soluble nickel salt, such as nickel chloride or nickel sulfate, with potassium cyanide solution:



The product is a tetrahydrate, $\text{Ni}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$, which on heating at 200°C yields yellow-brown anhydrous salt, $\text{Ni}(\text{CN})_2$.

Reactions

Nickel cyanide is practically stable in dilute acids at ordinary temperatures. Although the compound is water insoluble, it reacts with excess cyanide

ions in solution to form yellow tetracyanonickelate(II), $[\text{Ni}(\text{CN})_4]^{2-}$ anion:



Alkali metal salts of such tetracyanonickelate(II) anion may be crystallized from such solutions as hydrates, $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ upon evaporation of the solution. In strong cyanide solution, a pentacyano complex anion, red pentacyanonickelate(II), $[\text{Ni}(\text{CN})_5]^{3-}$ forms. Strong acids decompose cyanonickelate salts, precipitating nickel cyanide.

Cyanonickelate(II) may be reduced to red cyanonickelate(I) ion in solution by nascent hydrogen. Red potassium cyanonickelate(I), $\text{K}_2[\text{Ni}(\text{CN})_3]$ has been isolated. X-ray structure indicates that this compound is a binuclear complex, potassium tetracyano- μ -dicyanonickelate(I), $\text{K}_4[(\text{CN})_2\text{Ni}(\text{CN})_2\text{Ni}(\text{CN})_2]$.

Analysis

Elemental composition: Ni 53.00%, C 21.69%, N 25.30%. The compound may be identified by x-ray and selective chemical reactions with cyanide ions. Nickel may be analyzed in an acidified aqueous solution after it is solubilized with concentrated nitric acid or aqua regia (See Nickel).

Toxicity

The compound is toxic by ingestion.

NICKEL HYDROXIDE

[12054-48-7]

Formula: $\text{Ni}(\text{OH})_2$; MW 92.708; also forms a stable monohydrate, $\text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O}$ [36897-37-7], MW 110.72

Uses

Nickel hydroxide is used to prepare nickel salts and nickel catalysts; and in the manufacture of nickel-cadmium batteries.

Physical Properties

Green hexagonal crystal; density 4.10 g/cm³; decomposes to NiO on heating at 230°C; insoluble in water; K_{SP} 5.47×10^{-16} ; monohydrate is insoluble in water but soluble in dilute acids and ammonia.

Thermochemical Properties

ΔH_f°	-126.60 kcal/mol
ΔG_f°	-106.88 kcal/mol
S°	21.03 cal/degree mol

Preparation

Nickel hydroxide is prepared by various methods, mostly involving reaction

of caustic soda or caustic potash with a soluble nickel salt. Thus, treating nickel sulfate solution with sodium hydroxide forms a voluminous green gel. The gel crystallizes on prolonged storage. Alternatively, the solution on neutralization forms a fine precipitate of nickel hydroxide. Nickel nitrate also is used as starting material to prepare nickel hydroxide. Its aqueous solution, on treatment with sodium or potassium hydroxide, yields a gelatinous precipitate of nickel hydroxide which may be extracted with hot alcohol to form high purity product.

Nickel hydroxide in high purity is prepared by an electrolytic process using metallic nickel as the anode and nickel nitrate solution as the electrolyte. Nickel hydroxide is electrodeposited at an inert cathode.

Analysis

Elemental composition: Ni 63.32%, H 2.17%, O 34.51%. The hydroxide may be digested with nitric acid, diluted appropriately, and analyzed for nickel by various instrumental methods (See Nickel). Also, water content may be measured by TGA or DTA method after decomposing the hydroxide at 230°C. The residue NiO may be characterized by x-ray and other methods (See Nickel Oxide).

NICKEL NITRATE

[13138-45-9]

Formula: $\text{Ni}(\text{NO}_3)_2$; MW 182.72; occurs as hexahydrate at ordinary temperatures, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [13478-00-7], MW 290.79

Synonyms: nickel(II) nitrate; nickelaus nitrate

Uses

Nickel nitrate is used in the preparation of nickel-impregnated catalysts. It also is used to make nickel plates in nickel-cadmium batteries. Other applications are in ceramics to produce brown colors and in preparing nickel oxide.

Physical Properties

The hexahydrate forms emerald green monoclinic crystals; hygroscopic; density 2.05 g/cm³; isomorphous with corresponding cobalt salt; melts at 56.7°C; loses water on heating, decomposing to nickel oxide; very soluble in water; aqueous solution acidic; soluble in ethanol.

Preparation

Nickel nitrate hexahydrate may be prepared by several methods based on the reaction of dilute nitric acid on nickel powder, nickel oxide or nickel carbonate. The reaction is exothermic and requires controlled cooling during production. The hexahydrate can be dehydrated to anhydrous salt by treatment with fuming nitric acid.

Analysis

Elemental composition (anhydrous $\text{Ni}(\text{NO}_3)_2$): Ni 32.13%, N 15.33%, O 52.54%. The percent composition of Ni, NO_3^- , and H_2O in the hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is 20.18%, 42.65% and 37.17%, respectively. The hexahydrate may be identified by TGA, DTA and x-ray techniques. Nickel may be measured in an appropriately diluted aqueous solution by AA, ICP and other instrumental techniques. Nitrate ion, NO_3^- may be measured in an appropriately diluted solution by ion chromatography or with a nitrate ion-selective electrode.

NICKEL OXIDE

[1313-99-1]

Formula: NiO ; MW 74.692

Synonyms: nickel(II) oxide; nickelous oxide; green nickel oxide; nickel protoxide.

Occurrence

The oxide occurs in nature in the mineral, bunsenite.

Uses

Nickel oxide is used in the ceramic industry for making frit, ferrites, and coloring porcelain. The oxide in sinter form is used in the production of nickel-steel alloys. It supplies oxygen to the melt for removal of carbon as carbon dioxide. Some other important uses of nickel oxide include preparation of many nickel salts, specialty chemicals, and nickel catalysts. It also is used as an electrode in fuel cells.

Physical Properties

Green cubic crystals; transforms to a grayish black octahedral form, known as black oxide, when strongly ignited; black oxide has a metallic luster; density of green oxide is 6.72 g/cm^3 ; Mohs hardness 5.5; melts at 1955°C ; insoluble in water; soluble in acids at ordinary temperatures; black form dissolves in hot acids.

Preparation

Nickel oxide is prepared by heating pure nickel powder with oxygen at a temperature above 400°C . In some commercial processes, green nickel oxide is made by heating a mixture of nickel powder and water in air at $1,000^\circ\text{C}$. Adding some nickel oxide to the above mixture enhances the rate of reaction. An alternative method of preparation of the green oxide involves thermal decomposition of an oxo acid salt of nickel at elevated temperatures. Thus, nickel nitrate, nickel sulfate or, more conveniently, nickel carbonate when heated at $1,000^\circ\text{C}$, yields the green oxide. The black oxide, on the other hand, is produced at a lower temperature from incomplete calcination of the carbonate or nitrate salt at 600°C . The oxygen content of the black form is slight-

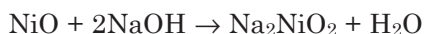
ly greater than its green counterpart.

Reactions

Several nickel salts are obtained by reactions of nickel oxide with mineral acids. Thus, the reaction of black nickel oxide with hot dilute sulfuric acid forms nickel sulfate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. Similarly, dilute nitric acid, hydrochloric, and hydrobromic acids when heated react with the black form of nickel oxide to yield corresponding nickel salts as hexahydrates.

Heating nickel oxide with hydrogen, carbon, or carbon monoxide reduces it to metallic nickel.

Nickel oxide combines with sodium or potassium hydroxide at elevated temperatures ($>700^\circ\text{C}$), forming sodium or potassium nickelate; i.e., K_2NiO_2 :



Analysis

Elemental composition: Ni 78.58%, O 21.42%. Nickel may be analyzed in a diluted solution of the oxide in nitric acid by AA, ICP and other instrumental methods. The oxide may be identified from its physical properties and by x-ray diffraction.

NICKEL PHOSPHATE

[10381-36-9]

Formula: $\text{Ni}_3(\text{PO}_4)_2$; MW 366.07; forms a stable heptahydrate, $\text{Ni}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$ [14396-43-1]

Synonyms: nickel orthophosphate, trinickel orthophosphate

Uses

Nickel phosphate is used in coating steel and in treatment of metal surfaces. It also is used to prepare the pigment, nickel yellow for oil and water colors. The compound is used in electroplating also.

Physical Properties

The heptahydrate is a light apple green powder; decomposes on heating; insoluble in water; soluble in acids and ammonia solution.

Preparation

Nickel phosphate heptahydrate is obtained as a pale green flocculent precipitate when disodium hydrogen phosphate, Na_2HPO_4 is added to a nickel salt solution. The precipitate is air-dried.

Analysis

Elemental composition (of anhydrous $\text{Ni}_3(\text{PO}_4)_2$): Ni 48.11%, P 16.92%, O 34.97%. The water of crystallization in the hydrated salt is determined by DTA and TGA methods. Nickel content may be determined by AA or ICP-AES

analysis of the nitric acid extract of nickel phosphate.

NICKEL SULFAMATE

[13770-89-3]

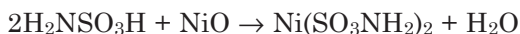
Formula: $\text{Ni}(\text{SO}_3\text{NH}_2)_2 \cdot 4\text{H}_2\text{O}$; MW 322.93; occurs as a tetrahydrate.

Uses

Nickel sulfamate is used as an electrolyte in nickel electroplating systems.

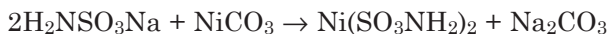
Preparation

Nickel sulfamate is prepared by heating an aqueous solution of sulfamic acid, $\text{H}_2\text{NSO}_3\text{H}$, with fine nickel powder or black nickel oxide under controlled conditions:



At ordinary temperatures, sulfamic acid hydrolyzes slowly forming ammonium bisulfite. However, when heated it hydrolyzes rapidly forming sulfuric acid. Therefore nickel sulfamate should be prepared rapidly before any sulfamic acid hydrolysis occurs due to longer contact time with water.

Nickel sulfamate also can be prepared by the action of sodium sulfamate on nickel carbonate:



Nickel sulfamate is usually not isolated from its product mixtures. The product solution is sold for commercial applications.

Analysis

Elemental composition: Ni 18.16%, S 19.86%, H 3.75%, N 8.67%, O 49.54%. The composition of water in nickel sulfamate tetrahydrate is 22.31%. Nickel content in solution may be determined by AA, ICP and other instrumental techniques.

NICKEL SULFATE

[7786-81-4]

Formula: NiSO_4 ; MW 154.75; occurs as hexahydrate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ [10101-97-0], MW 262.85 and the heptahydrate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ [10101-98-1], MW 280.86

Occurrence and Uses

Nickel sulfate heptahydrate occurs in nature as the mineral morenosite.

Probably, the most important uses of nickel sulfate are as an electrolyte in nickel plating and electrorefining. Nickel sulfate also is used as a mordant in dyeing and printing textiles. Other uses are in the preparation of many nickel compounds and nickel catalysts; as a reducing agent; for imparting nickel coating or flashing on steel surface; and for blackening zinc and brass.

Physical Properties

The anhydrous salt is a yellow cubic crystalline solid; density 3.68 g/cm³; decomposes at 848°C; readily dissolves in water; insoluble in ethanol, ether and acetone.

The hexahydrate, NiSO₄•6H₂O occurs in two crystalline forms, a blue tetragonal alpha-allotrope and an emerald green monoclinic beta form. The blue alpha form converts to green beta above 53.3°C. The beta form is isomorphous with magnesium sulfate hexahydrate, MgSO₄•6H₂O. Density of hexahydrate is 2.07 g/cm³; refractive index 1.511; loses water on heating; very soluble in water; also very soluble in ethanol and ammonia solution.

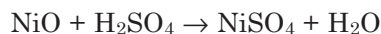
The heptahydrate, NiSO₄•7H₂O, forms green rhombohedral crystals; refractive index 1.467; density 1.948 g/cm³; loses water on heating; highly soluble in water (about 75 g/100mL at 15°C); soluble in alcohol.

Thermochemical Properties

ΔH_f° (anhydrous NiSO ₄)	-208.6 kcal/mol
ΔH_f° (alpha-NiSO ₄ •6H ₂ O)	-641.2 kcal/mol
ΔH_f° (beta-NiSO ₄ •6H ₂ O)	-638.7 kcal/mol
ΔH_f° (NiSO ₄ •7H ₂ O)	-711.4 kcal/mol
ΔG_f° (anhydrous NiSO ₄)	-181.6 kcal/mol
ΔG_f° (alpha-NiSO ₄ •6H ₂ O)	-531.8 kcal/mol
ΔG_f° (NiSO ₄ •7H ₂ O)	-588.8 kcal/mol
S° (anhydrous NiSO ₄)	22.0 cal/degree mol
S° (alpha-NiSO ₄ •6H ₂ O)	79.9 cal/degree mol
S° (NiSO ₄ •7H ₂ O)	90.6 cal/degree mol
C _p (anhydrous NiSO ₄)	33.0 cal/degree mol
C _p (alpha-NiSO ₄ •6H ₂ O)	78.4 cal/degree mol
C _p (NiSO ₄ •7H ₂ O)	87.1 cal/degree mol

Preparation

Nickel sulfate can be made by several methods. It is prepared by dissolving nickel metal, its oxide, or its carbonate in sulfuric acid. In such methods, powdered metal or black nickel oxide is added to hot dilute sulfuric acid, or nickel carbonate is added to dilute sulfuric acid at ambient temperature:



Impurities may be precipitated by treating the diluted solution with barium carbonate. Evaporation followed by cooling crystallizes hexahydrate in

two modifications: blue tetragonal crystals obtained between 31.5 and 53.3°C, and above 53.3°C green monoclinic crystals form. The heptahydrate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, crystallizes at ordinary temperatures from pure aqueous solutions.

Nickel sulfate also can be produced in large-scale by gas phase reaction of nickel tetracarbonyl, sulfur dioxide, and oxygen at 100°C:

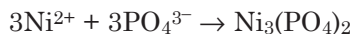


Reactions

Hydrated nickel sulfate on heating at 103°C loses all of its water molecules. At 848°C, the anhydrous sulfate decomposes to nickel oxide and sulfur trioxide:



Nickel sulfate is used in preparing many insoluble nickel salts. In aqueous solutions, such insoluble nickel compounds precipitate; e.g.,



Nickel sulfate forms double salts with ammonium or alkali metal sulfates. For example, blue-green hydrated ammonium nickel sulfate, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, crystallizes from a mixed solution of nickel sulfate and ammonium sulfate. Such double sulfates are isomorphous to corresponding alkali metal or ammonium double sulfates of iron, cobalt, magnesium, zinc, and other bivalent metals.

Analysis

Elemental composition (in anhydrous NiSO_4): Ni 37.93%, S 20.72%, O 41.35%. The water content in hexahydrate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, and heptahydrate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, are 41.12% and 47.98%, respectively. Nickel may be analyzed in aqueous solution by AA, ICP, and other instrumental methods (see Nickel). Sulfate may be analyzed in aqueous solution by ion chromatography. The compound may be characterized by x-ray methods.

NICKEL SULFIDE

[1314-04-1]

Formula: NiS ; MW 90.75; the compound may have nonstoichiometric compositions.

Synonyms: nickel monosulfide; nickel(II) sulfide; millerite.

Occurrence and Uses

Nickel sulfide occurs in nature as mineral millerite. Its principal use is as a source material for making nickel metal.

Physical Properties

Trigonal crystalline solid or amorphous powder; mineral millerite has a yellow metallic luster; color varies from yellow to brownish black; density 5.30 to 6.65 g/cm³; exhibits three allotropic modifications: (1) the acid-soluble amorphous alpha form obtained from nickel salt solution by precipitation with ammonium sulfide, (2) the alpha form rapidly transforms to a crystalline beta form as a brown colloidal dispersion upon exposure to air, and (3) a rhombohedral gamma modification found native as mineral millerite, which also can be prepared artificially under certain conditions.

Gamma-NiS slowly converts to beta-NiS in solution. Beta form probably is richer in sulfur than alpha and gamma modifications and therefore they could have varying stoichiometric compositions.

Nickel sulfide melts at 797°C and is insoluble in water (3.6 mg/L at 18°C; soluble in concentrated nitric acid and potassium hydrogen sulfide solution; slightly soluble in alcohol.

Thermochemical Properties

ΔH_f°	-19.6 kcal/mol
ΔH_f° (precipitated NiS)	-18.5 kcal/mol
ΔG_f°	-19.0 kcal/mol
S°	12.66 cal/degree mol
C_p	11.26 cal/degree mol

Preparation

Nickel sulfide is mined directly from natural deposits. Also, it can be prepared in the laboratory by precipitation from an aqueous solution of a nickel salt with ammonium sulfide, (NH₄)₂S, or by precipitation from an acetic acid solution with hydrogen sulfide. While the aqueous solution method yields an amorphous product (alpha-NiS) which rapidly changes on exposure to air and contact with the solution to a brown crystalline sulfide (beta-NiS), the acid solution method forms only crystalline beta-NiS.

Nickel sulfide also can be prepared by reacting nickel powder with molten sulfur.

Analysis

Elemental composition: Ni 64.68%, S 35.33%. The compound may be identified by x-ray crystallographic and physical properties. Nickel may be measured in nitric acid extract by AA or ICP methods (See Nickel).

NICKEL TETRACARBONYL

[13463-39-3]

Formula: Ni(CO)₄; MW 170.73; a zerovalent nickel compound

Synonym: nickel carbonyl

History and Uses

Nickel tetracarbonyl was prepared first in 1888 by Mond and Langer by passing carbon monoxide over finely divided nickel. It is the most important zero valent compound of nickel and is used industrially to make high-purity nickel powder and pellets and to produce nickel coatings on steel.

Physical Properties

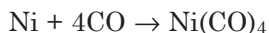
Colorless volatile liquid; diamagnetic; flammable; burns with a bright luminous flame; density 1.319 g/mL; freezes at -25°C ; boils at 43°C ; vapor pressure 320.6 torr at 20°C ; vapor density 5.89 (air=1); critical temperature about 200°C ; critical pressure 30 atm; practically insoluble in water, 180 mg/L at 10°C ; miscible with most organic solvents including ethanol, acetone, and benzene; soluble in nitric acid and aqua regia.

Thermochemical Properties

ΔH_f° (liq)	-151.3 kcal/mol
ΔH_f° (gas)	-144.1 kcal/mol
ΔG_f° (liq)	-140.6 kcal/mol
ΔG_f° (gas)	-140.4 kcal/mol
S° (liq)	74.9 cal/degree mol
S° (gas)	98.1 cal/degree mol
C_p (liq)	48.9 cal/degree mol
C_p (gas)	34.7 cal/degree mol

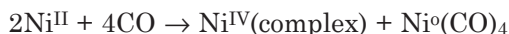
Preparation

Nickel tetracarbonyl is made by passing carbon monoxide over finely divided nickel at 50 to 100°C . (The finely divided nickel is obtained from reduction of nickel oxide by hydrogen below 400°C .)



In several commercial processes the reaction is carried out at a temperature of 200°C under 400 atm carbon monoxide pressure for obtaining high yield of nickel tetracarbonyl and also to prevent thermal dissociation.

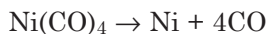
Nickel tetracarbonyl may be prepared in the laboratory by the Hieber process, a disproportion reaction of several nickel compounds of organic thio acids, such as nickel(II) phenyldithiocarbamate, $(\text{C}_6\text{H}_5\text{—NH—C(=S)—S})_2\text{Ni}$, with carbon monoxide under controlled conditions. In such disproportionation reactions, the divalent nickel ion converts to a tetravalent nickel complex (Hieber. H. 1952. *Z.anorg.Chem.*, 269, pp. 28). The overall reaction is:



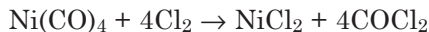
Reactions

Nickel tetracarbonyl decomposes to metallic nickel and carbon monoxide when heated at 180 to 200°C . Thus, when its vapors are passed through a tube heated at 180 to 200°C , a brilliant mirror of metallic nickel is deposited

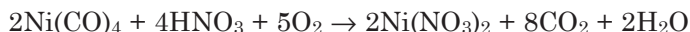
on the tube:



Reaction with chlorine yields phosgene (carbonyl chloride) and nickel chloride:



Concentrated nitric acid and other oxidizing agents decompose nickel tetracarbonyl forming their nickel salts, carbon dioxide and water:



Nickel tetracarbonyl reacts with nitric oxide in the presence of moisture, forming a deep blue compound, nickel nitrosyl hydroxide, Ni(NO)OH .

Analysis

Elemental composition: Ni 34.38%, C 28.13%, O 37.48%. The compound may be identified and measured quantitatively by GC/MS. An appropriately diluted solution in benzene, acetone, or a suitable organic solvent may be analyzed. Alternatively, nickel tetracarbonyl may be decomposed thermally at 200°C, the liberated carbon monoxide purged with an inert gas, and transported onto the cryogenically cooled injector port of a GC followed by analysis with GC-TCD on a temperature-programmed column. Nickel may be analyzed by various instrumental techniques following digestion of the compound with nitric acid and diluting appropriately (See Nickel).

Hazard

Nickel tetracarbonyl is both a fire and explosion hazard and is a highly toxic compound. It is a volatile flammable liquid with a flash point (closed cup) -4°F (-18°C) and forms explosive mixtures with air. It explodes when heated in oxygen or air or when it is dry and shaken vigorously with oxygen in the presence of mercury or mercuric oxide.

The carbonyl is toxic by all routes of exposure, manifesting both immediate and delayed effects. Symptoms from breathing its vapors are headache, dizziness, giddiness, nausea, vomiting, and hallucinations. Prolonged inhalation can cause rapid breathing, congestion of the lungs, and brain and liver injury. Ingestion can be fatal. It induces tumors in lungs and livers of experimental animals.

Inhalation LC_{50} in mice over a 30-minute exposure period is 0.067 mg/L and the oral LD_{50} in rats is about 60 mg/kg.

NIOBIUM

[7440-03-1]

Symbol: Nb; atomic number 41; atomic weight 92.906; a Group VB (Group 5) element; a transition metal in the triad of vanadium and tantalum; also,

known as columbium; electron configuration $[\text{Kr}]4d^45s^1$; valence states +3, +4 and +5; the most common oxidation state +5; atomic radius 1.47Å; ionic radius, Nb^{5+} 0.68Å; atomic volume 10.8 cm³/mol; ionization potential 6.77 eV; one stable natural isotope, Nb-93; several radioactive isotopes are known in the mass range 88-92 and 94-101.

History and Occurrence

The element was discovered in 1801 by British chemist Charles Hatchett during analysis of a black mineral sample from the British Museum, originally sent in 1753 from Connecticut. He named the element *columbium*, after the country of its origin, Columbia (United States). In 1844, Rose announced the discovery of a new element which he named as *niobium*, in honor of Niobe, the daughter of Tantalus, the mythological Goddess of Tears. Later, it was established that Hatchett's columbium and Roses' niobium were the same element. Both names remained in use for more than one hundred years. In 1949 at the Fifteenth International Union of Chemistry Congress held at Amsterdam, the name niobium was officially adopted as the international name.

Niobium was prepared in the metallic state for the first time by Blomstrand in 1866, later by Moissan, and still later, by Goldschmidt. While Blomstrand reduced niobium chloride with hydrogen to form niobium, Moissan and Goldschmidt reduced the oxide with carbon (in an electrical furnace) and aluminum powder, respectively.

Niobium occurs naturally in several minerals, mostly associated with tantalum and many rare earth elements. The metal is never found in free elemental form. It occurs mostly as hydroxide, silicate, or borate or as its oxy salt, niobate, which is mostly associated with isomorphous tantalate. The principal niobium minerals are pyrochlore, loparite, and koppite all of which contain titanium together with calcium and other metals, such as cerium. They are complex hydroxide minerals and their composition may vary with place. Another type of niobium mineral is the niobates-tantalates mixed ores of Nb_2O_6 — Ta_2O_6 or of compositions $(\text{Nb},\text{Ta})_2\text{O}_6$. Such ores usually contain iron and sometimes manganese which partially replaces iron. A typical example is an isomorphous admixture of $\text{Fe}(\text{NbO}_3)_2$ — $\text{Fe}(\text{TaO}_2)_2$. Many impurity metals, such as tungsten, titanium, and tin are also found in these ores.

The abundance of niobium in the earth's crust is estimated to be in the range 20 mg/kg and its average concentration in sea water is 0.01 mg/L. The metal also is found in the solar system including the lunar surface. Radionuclides niobium-94 and -95 occur in the fission products of uranium-235.

Uses

Niobium is a very important metal in both ferrous and nonferrous metallurgy. As an additive to alloys or when alloyed with other metals niobium imparts high mechanical strength, high electrical conductivity, and ductility to alloys. It enhances corrosion resistance of most alloys. The metal and several of its alloys exhibit superconductivity. Niobium is used as an additive in

the manufacture of most high strength, low alloy carbon steels and microalloyed steels that are used in the construction of oil and gas pipelines, bridges, buildings, concrete bars, and automobiles.

Niobium also is added to nickel- and cobalt-based superalloys and is a component of zirconium, titanium and tungsten alloys.

Other applications of niobium are in electronic and propulsion devices, in electrodes; in catalysis; and in vacuum tubes and high-pressure sodium vapor lamps.

Physical Properties

Grayish, soft metal with a white luster on polished surfaces; ductile and very malleable at room temperature; also highly ductile at cryogenic temperatures; body-centered cubic crystals; density 8.66 g/cm³ at 20°C; melts at 2,468±10°C; vaporizes at 5,127°C; electrical resistivity 13.2 microhm-cm at 20°C; becomes superconducting at 9.15K; thermal neutron-capture cross section 1.1 barns; insoluble in water; insoluble in hydrochloric acid, nitric acid and aquaregia; soluble in hydrofluoric acid; soluble in fused alkali hydroxide.

Thermochemical Properties

ΔH_f°	0.0
ΔH_f° (gas)	172.76 kcal/mol
ΔG_f°	0.0
ΔG_f° (gas)	173.50 kcal/mol
S°	8.70 cal/degree mol
S° (gas)	44.49 cal/degree mol
C_p	5.88 cal/degree mol
C_p (gas)	7.21 cal/degree mol
ΔH_{fus}	6.318 kcal/mol
ΔH_{vap}	166.6 kcal/mol
Thermal conductivity	0.52 watts/cm°C
Coeff. linear expansion	0.064x10 ⁻⁶ /°C at 25°C
$\Delta H_{combstn}$	226.8 kcal/mol

Production

There are several processes for extracting and refining niobium from its ores. (Payton, P.H. 1981. Niobium and Niobium Compounds. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd. ed., Vol, 15, pp. 820-827. New York: Wiley Interscience). The process of choice depends on nature of the ore and end use intended for the metal. Some common steps in these recovery processes involve ore preconcentration, breaking or opening the ore, obtaining pure niobium compounds, reduction of niobium compounds to niobium metal, purification or refining metal and fabrication. If niobium is extracted from a niobium-tantalum ore, the most important step is separation of niobium from tantalum, both of which are chemically very similar.

Ferroniobium can be produced from the ore pyrochlore in batch process by thermal reduction in a refractory-lined steel or preferably an electric furnace reactor. Aluminum powder is used as a reducing agent. A mixture of niobium

ore, iron oxide, aluminum powder, lime, and an oxidizer such as sodium chlorate, is fed into the reactor. The mixture is ignited electrically. Molten ferro-niobium formed is collected at the reactor bottom and low density slags containing impurities float on top of the molten alloy. Some other metal oxides present in the ore or in the reactant feed are also reduced by aluminum under ignition. Such metals generated in small amounts may incorporate into ferro-niobium and include silicon, tantalum, titanium, tin and lead. This fused mass also contains minor quantities of aluminum.

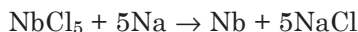
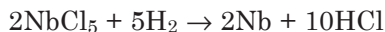
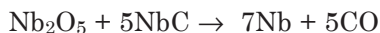
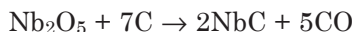
Ore-opening, a key step in the recovery of niobium is carried out by several methods. Some major methods are: (1) Heating the ore, niobates, or niobates-tantalates with hydrofluoric acid (70-80% by weight) and nitric acid. This method is not economical for pyrochlore-type ores that have high contents of alkali and alkaline earth oxides for which they require high acid consumption. (2) Fusion with sodium hydroxide at elevated temperatures is another common method of ore opening. Fusion is carried out in an iron retort at a temperature between 500 to 800°C. Pyrochlore and columbites are converted to insoluble niobates. Fusion products are leached with water and filtered to separate insoluble niobates. Niobates are then converted to niobic acid by treatment with hydrochloric acid and separated by filtration. (3) Pyrochlore and columbites alternatively may be digested with concentrated sulfuric acid at 300 to 400°C in an iron crucible. Sulfate complexes of niobium formed are hydrolyzed by boiling with water to yield white colloidal precipitate of niobic acid. (4) Ore crushed to finely ground state may be heated with carbon at high temperatures to produce metal carbides. This method is applicable to pyrochlore type ores. The reaction is initiated at 950°C and carried out at 1,800°C for completion. The product mixture containing carbides of niobium, tantalum and titanium is leached with hydrochloric acid to separate most acid-soluble materials. Carbide mixture is then dissolved in hydrofluoric acid converting them to respective fluorides. Carbides alternatively may be ignited in air or oxygen to convert them to oxides. (5) Another ore-opening process usually applied to columbites involves chlorination. For this method, ore is crushed and mixed with carbon and heated with chlorine gas at 500 to 1,000°C. Niobium and other metals form their chlorides, which are volatile and can be separated by fractional condensation. Niobium, aluminum and iron form niobium pentachloride, aluminum chloride and iron(II)- and iron(III) chlorides, respectively. These chlorides and the chlorides of impurity metals that are formed are transported over a column of sodium chloride pellets at 400°C for separation. While more volatile chlorides pass through the condenser, iron and aluminum form low melting eutectic compounds and drain from the bottom of the column. Niobium pentachloride is selectively condensed.

Separation of niobium from tantalum and impurity metals is the most important step in its extraction from the ore. It may be achieved by several methods that include solvent extraction, ion exchange, fractional crystallization, fractional sublimation, and other techniques. Solvent extraction is applied mostly in several large-scale commercial processes. Although the classical fractional crystallization method forms effective separation, it is a tedious

process. Ion exchange techniques provide more effective removal of impurities than the solvent extraction methods. They are applied most often to produce high purity niobium and tantalum in small quantities. In solvent extraction methods, various acids are used in combination with hydrofluoric acid. An effective organic solvent for such solvent extraction is methyl isobutyl ketone (MIBK). Extraction is based on the principle that solubility of niobium and other metals varies with acid strength. Thus, in such extractions, pH is adjusted to obtain proper acidic conditions. There are also several variations in solvent extraction processes. Often ammonia is added to the niobium-bearing extract to precipitate niobium as oxyfluoride. The precipitate is then filtered, dried, and calcined to obtain high-purity niobium oxide. Another method involves addition of potassium fluoride to the extract to obtain a niobium potassium double fluoride. Recovery processes based on chlorination of the ore also utilize solvent extraction techniques. Chlorination at elevated temperatures yields anhydrous chlorides of niobium together with tantalum and iron. The chloride mixture is dissolved in MIBK and/or other suitable organic solvents and extracted with hydrochloric acid. While tantalum partitions into HCl, niobium and iron remain in the organic phase. Boiling with 20% H_2SO_4 precipitates niobic acid, thus separating niobium from iron, which remains in solution.

Many earlier commercial processes were based on separating niobium from tantalum and other metals by fractional crystallization. This method involves adding excess potassium fluoride to a solution of niobium ores in hydrofluoric acid. This forms complex fluorides and oxyfluorides of niobium, tantalum, and titanium of compositions $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$, K_2TaF_6 and $\text{K}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$, respectively. These complex salts are dissolved in 3% HF. Increasing concentrations of HF converts niobium oxyfluoride to K_2NbF_7 and KNbF_6 . Out of these three complex salts, niobium complex is most soluble in HF, while that of tantalum is least soluble. Thus, by appropriate control of temperatures and concentrations of HF and potassium fluoride (which suppresses solubility of these complexes), less soluble tantalum complex may be crystallized, leaving behind niobium complex in solution.

High purity grade metal may be produced by reduction of niobium pentoxide, Nb_2O_5 or pentachloride, NbCl_5 at elevated temperatures ranging from 1400 to 2000°C and often under vacuum using various reducing agents, such as carbon, hydrogen, sodium and other substances:



Reactions

At ordinary temperatures niobium does not react with most chemicals.

However, the metal is slowly attacked by hydrofluoric acid and dissolves. Also, at ordinary temperatures, it is attacked by hydrogen fluoride and fluorine gases, forming niobium pentafluoride, NbF_5 .

The metal reacts with chlorine at 300°C forming niobium pentachloride, NbCl_5 . It reacts with hot concentrated hydrochloric acid, also forming the pentachloride. Niobium dissolves in hot concentrated sulfuric acid at 170°C . Fused alkalis such as caustic soda and caustic potash attack niobium, embrittling the metal.

Niobium is oxidized by air at 350°C , first forming pale yellow oxide film of increasing thickness, which changes its color to blue. On further heating to 400°C , it converts to a black film of niobium dioxide, NbO_2 [12034-59-2]. Niobium forms three oxides: the cubic monoxide, NbO [12034-57-0]; the tetragonal dioxide, NbO_2 [12034-59-2]; and the monoclinic pentoxide, Nb_2O_5 [1313-96-8]. These oxides are obtained by heating Nb metal powder at very high temperatures. Reaction of niobium powder with niobium dioxide in compressed argon at $1,700^\circ\text{C}$ yields grayish niobium monoxide:



Similarly, heating the metal powder with pentoxide at $1,100^\circ\text{C}$ forms bluish-black dioxide:



Niobium absorbs hydrogen at 250°C , forming a stable interstitial solid solution. The reaction is exothermic. X-ray studies indicate a hydride, $\text{NbH}_{0.85}$. The hydride decomposes when heated at 500°C .

Niobium metal absorbs nitrogen, similar to hydrogen, forming interstitial solid solution. The absorption occurs at 300°C and the solubility of nitrogen in the metal is directly proportional to the square root of the partial pressure of nitrogen. The reaction is exothermic and the composition of such interstitial solid solution varies with the temperature. When the metal is heated with nitrogen at temperatures between 700 to $1,100^\circ\text{C}$, the product is niobium nitride, Nb_2N or $(\text{NbN}_{0.5})$ [12033-43-1]. When heated with ammonia at these temperatures, niobium forms this nitride. Another niobium nitride exists, NbN [24621-21-4], with a face-centered cubic crystalline structure.

Niobium combines with carbon, boron, silicon and other elements at very high temperatures, forming interstitial binary compounds of varying compositions. With carbon, it forms niobium carbide having compositions varying from $\text{NbC}_{0.7}$ to NbC [12069-94-2]. With boron, the products are orthorhombic niobium boride, NbB [12045-19-1], and the hexagonal diniobium diboride, Nb_2B_2 [12007-29-3].

Analysis

Niobium content in its ores, alloys or compounds may be measured quantitatively by dissolving the solid samples into aqueous phase followed by x-ray fluorescence, colorimetry, or gravimetry measurement. Samples may be dis-

solved in hydrofluoric acid or in its combination with nitric acid. Alternatively, niobium may be extracted into aqueous phase by fusion with caustic soda, caustic potash, or potassium pyrosulfate after which the fused mass is leached with water. Niobium may be separated from tantalum and other interfering substances by solvent extraction or ion exchange techniques. The metal forms water-soluble colored complexes with ascorbic acid and 5-nitrosalicylic acid or water-insoluble colored complexes with tannin, pyrocatechol, Cupferron, and other complexing agents for colorimetric measurements.

NIOBIUM PENTACHLORIDE

[10026-12-7]

Formula: NbCl_5 ; MW 270.17

Synonyms: columbium pentachloride; niobium(V) chloride

Uses

Niobium pentachloride is used in making niobium metal and several niobium compounds.

Physical Properties

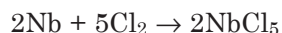
Yellow monoclinic crystals; deliquesces; density 2.75 g/cm^3 ; decomposes in moist air with the evolution of HCl ; melts at 204.7°C ; vaporizes at 254°C ; decomposes in water; soluble in alcohol, hydrochloric acid, chloroform and carbon tetrachloride.

Thermochemical Properties

ΔH_f°	-190.6 kcal/mol
ΔG_f°	-163.3 kcal/mol
S°	$50.3 \text{ cal/degree mol}$
C_p	$35.4 \text{ cal/degree mol}$

Preparation

Niobium pentachloride is obtained as an intermediate during extraction of niobium from its ores (see Niobium). Also, the pentachloride is obtained readily by direct chlorination of niobium metal at 300 to 350°C :



The pentachloride also may be made by chlorination of niobium pentoxide in the presence of carbon at 300°C . The products, however, contain small amounts of niobium oxide trichloride, NbOCl_3 .

Analysis

Elemental composition: Nb 34.39%, Cl 65.61%. The compound may be decomposed in water carefully and the aqueous solution appropriately diluted.

ed and measured for niobium by x-ray fluorescence or colorimetry (See Niobium). Chloride ion may be measured by ion chromatography or titration with a standard solution of silver nitrate using potassium chromate as an indicator. An appropriately diluted carbon tetrachloride solution of niobium pentachloride may be analyzed by GC/MS. The solution may be injected directly onto a semipolar capillary GC column and identified from the mass spectra. The characteristic mass ions for compound identification are 93 and 270.

NIOBIUM PENTAFLUORIDE

[7783-68-8]

Formula: NbF₅; MW 187.90

Synonyms: columbium pentafluoride; niobium(V) fluoride

Uses

Niobium pentafluoride is used in making other fluoro compounds of niobium.

Physical Properties

Colorless monoclinic crystals; hygroscopic; density 3.293 g/cm³; melts at 72°C; vaporizes at 236°C; hydrolyzes in water forming hydrofluoric acid and fluoroniobic acid, H₂NbOF₅; soluble in alcohol, slightly soluble in chloroform, carbon disulfide and sulfuric acid.

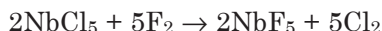
Thermochemical Properties

ΔH_f°	-433.5 kcal/mol
ΔG_f°	-406.1 kcal/mol
S°	38.3 cal/degree mol
C_p	32.3 cal/degree mol

Preparation

Niobium pentafluoride is obtained as an intermediate during the recovery of niobium metal from its ores (See Niobium). It also can be prepared by direct fluorination of niobium metal at 250 to 300°C, either by fluorine gas or anhydrous hydrofluoric acid. The pentafluoride vapors are condensed in a pyrex or quartz tube from which it is sublimed at 120°C under vacuum and collected as colorless crystals.

Also, niobium pentafluoride can be prepared by the reaction of fluorine with niobium pentachloride:



Analysis

Elemental composition: Nb 49.44%, F 50.56%. The compound is dissolved in water cautiously. The solution is diluted appropriately and analyzed for

niobium by x-ray fluorescence or colorimetry (see Niobium). The fluoride ion in aqueous solution may be measured by ion chromatography or a fluoride ion-selective electrode.

NIOBIUM PENTOXIDE

[1313-96-8]

Formula: Nb_2O_5 ; MW 265.81

Synonyms: niobium(V) oxide; diniobium pentaoxide; columbium pentaoxide

Uses

Niobium pentaoxide is used for preparing many niobium salts, including niobium carbide (Balke process). It also is used in the aluminothermic process in the production of niobium metal.

Physical Properties

White orthogonal crystals; density 4.60 g/cm³; melts at 1,512°C; insoluble in water; soluble in hydrofluoric acid.

Thermochemical Properties

ΔH_f°	-454.0 kcal/mol
ΔG_f°	-422.1 kcal/mol
S°	32.8 cal/degree mol
C_p	31.6 cal/degree mol
ΔH_{fus}	24.9 kcal/mol

Preparation

Niobium pentoxide is produced as an intermediate during recovery of Nb metal from ores (See niobium).

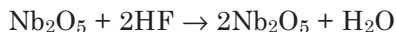
Also, the pentoxide may be produced by igniting niobium metal powder, niobium carbide, or niobium fluoride in oxygen.

Reactions

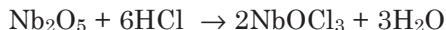
Niobium pentaoxide undergoes two important types of reactions, one is reduction to niobium metal or to lower oxides, and the other involves conversion of pentoxide to oxide trihalides when treated with halogens or halides. These reactions occur mostly at elevated temperatures. Reductions may be carried out by carbon, hydrogen, niobium carbide, niobium metal, and other reducing agents at elevated temperatures and often in vacuum:



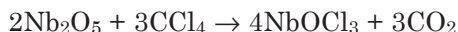
When treated with aqueous hydrofluoric acid followed by evaporation to dryness, niobium dioxide fluoride, NbO_2F [15195-33-2] is formed:



Niobium pentoxide reacts with hydrogen chloride gas at 400 to 700°C to form niobium oxide trichloride, NbOCl_3 [13597-20-1]:



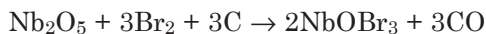
Reaction with carbon tetrachloride at elevated temperatures also yields the same product:



Pentaoxide also reacts with niobium pentachloride at elevated temperatures, forming the oxide trichloride:



Yellow-brown oxide called tribromide of niobium, NbOBr_3 [14459-75-7], is produced by reacting niobium pentoxide with bromine and carbon at 550°C:



Analysis

Elemental composition: Nb 69.90%, O 30.10%. The oxide is dissolved in HF-HNO_3 mixture and diluted appropriately. The solution is analyzed for niobium by x-ray fluorescence or colorimetry (See Niobium).

NITRIC ACID

[7697-37-2]

Formula: HNO_3 ; MW 63.01

History and Uses

Nitric acid was known to alchemists in ancient times. Cavendish in 1784 synthesized the acid by applying an electric spark to humid air. Earlier in 1776, Lavoisier determined that the acid contained oxygen. In 1798, Milner prepared nitric acid from ammonia along with nitrogen oxides by oxidation of ammonia vapor over red-hot manganese dioxide. In 1816, Gay-Lussac and Berthollet established its composition.

Nitric acid is one of the most important industrial chemicals in the world. Its largest use is in the fertilizer industry for producing various nitrate fertilizers. Such fertilizers include ammonium-, sodium-, potassium-, and calcium nitrates. Other major applications of nitric acid are in making nitrates and nitroorganics for use in explosives, gunpowder, and fireworks. Ammonium nitrate, nitroglycerine, nitrocellulose, and trinitrotoluenes are examples of such explosives, while barium and strontium nitrates are used in fireworks.

Another major application is in producing cyclohexanone, a raw material for adipic acid and caprolactam to produce nylon.

Nitric acid is a common laboratory reagent. It also is one of the most used oxidizing agents, applied in several organic and inorganic syntheses. Some synthetic applications of nitric acid include the production of diazo dyes, varnishes, lacquers, plastics, polyurethanes, and detergents. Other applications are in metal etching, ore extractions, pickling of stainless steel, rocket propellant, for processing nuclear fuel, as a solvent in aqua regia, for sample digestion in metal analysis by AA or ICP, and in preparing analytical standards.

Concentrated nitric acid used in commerce is not 100% pure nitric acid. It is the constant boiling mixture containing 68% pure acid.

Physical Properties

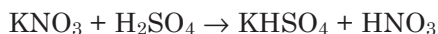
Colorless liquid; highly corrosive; refractive index 1.397 at 16.5°C; density 1.503 g/L; freezes at -42°C; boils at 83°C; completely miscible with water; forms a constant boiling azeotrope with water at 68.8 wt% nitric acid; the azeotrope has density 1.41 g/mL and boils at 121°C.

Thermochemical Properties

ΔH_f° (liq)	-41.61 kcal/mol
ΔH_f° (gas)	-32.28 kcal/mol
ΔH_f° (molar aq.)	-49.56 kcal/mol
ΔH_f° (liq)	-19.31 kcal/mol
ΔG_f° (gas)	-17.87 kcal/mol
ΔG_f° (molar aq.)	-26.61 kcal/mol
S° (liq)	37.19 cal/degree mol
S° (gas)	63.64 cal/degree mol
C_p (liq)	26.26 cal/degree mol
C_p (gas)	12.75 cal/degree mol
ΔH_{fus}	2.51 kcal/mol

Production

Nitric acid may be produced by several methods. In the laboratory, it is prepared by distilling a solution of potassium nitrate in concentrated sulfuric acid containing equal amounts (by weight) of each..

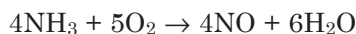


Nitric acid decomposes to nitrogen dioxide. Therefore, the temperature must be kept as low as possible. During this preparation, nitric acid condenses as a fuming liquid. The pure acid may be obtained when it is collected at -42°C, its freezing point. When nitric acid is collected by condensation at room temperature, it may decompose partially to nitrogen pentaoxide, N_2O_5 , which fumes in moist air. Early commercial processes were based on reaction of Chile saltpeter (NaNO_3) with sulfuric acid. Concentrated nitric acid was obtained by distilling the reaction mixture.

Nitric acid also may be obtained by rapid passage of air through an electric

arc. The method is based on Cavendish's first preparation of nitric acid. In this method, nitrogen and oxygen first combine to form nitric oxide. The gaseous product mixture usually containing about 2% nitric oxide is combined with excess oxygen to form nitrogen dioxide and nitrogen pentoxide. Dissolution of these gases in water forms nitric acid. The process, however, is expensive and unsuitable for commercial application.

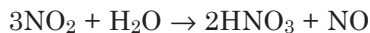
Currently, nitric acid is manufactured exclusively by catalytic oxidation of ammonia. Platinum or platinum-rhodium is an effective catalyst of this oxidation (Ostwald process). Three basic steps in such ammonia oxidation process are: (1) oxidation of ammonia to form nitric oxide:



The above reaction is rapid and shifts almost fully to the product side. (2) oxidation of nitric oxide to form nitrogen dioxide:

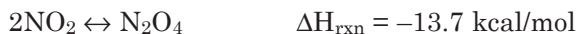


The above reaction also is rapid and goes almost to completion below 150°C. (3) dissolution of nitrogen dioxide in water:

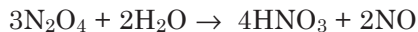


This reaction is moderately exothermic, releasing 32.4 kcal/mol.

Several mechanisms have been proposed for absorption of nitrogen dioxide in water. Nitrogen dioxide readily dimerizes to tetroxide, N_2O_4 , at low temperatures and increasing pressure.



Absorption of tetroxide in water also could form nitric acid and nitric oxide:



Several modifications in plant design and process conditions for ammonia oxidation processes have taken place in recent years. These variations are more or less based on operating pressures and temperatures, reduction of NO_x emission and other environmental regulations, and the desired plant production capacity.

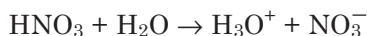
Nitric acid obtained in standard ammonia oxidation is usually 50 to 70% by weight aqueous solution. Pure nitric acid of 98-99% may be obtained either by extractive distillation or by direct strong nitric (DSN) processes. In the distillation method, concentrated nitric acid of 50-70% is distilled with 93% sulfuric acid in a steam-heated tower. Sulfuric acid acts as a dehydrating agent. The distilled nitric acid vapor is condensed to pure nitric acid, while sulfuric acid absorbing water from 50-70% nitric acid loses its strength to about 70% and collects at the bottom. The 70% sulfuric acid is concentrated back to 93%

for reuse by removal of water in a sulfuric acid concentrator.

In the DSN process, nitrogen tetroxide, N_2O_4 obtained from ammonia oxidation is absorbed by concentrated nitric acid in the presence of air or oxygen to yield pure nitric acid. Alternatively, N_2O_4 may be separated from the product gases of the ammonia oxidation process by refrigeration and then is treated with dilute nitric acid in air or oxygen.

Reactions

Reactions of nitric acid are of three types. First, those of a strong monobasic acid. When dissolved in water, it readily forms hydronium, H_3O^+ , and nitrate NO_3^- ions:



Second, it reacts vigorously with bases:



The ionic species that would be present in an aqueous solution when mixed with caustic soda solution are:



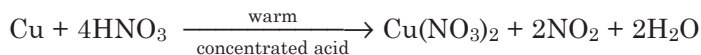
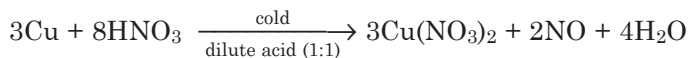
Evaporation of the solution will yield the salt sodium nitrate, NaNO_3 .

Third, the most important reactions of nitric acid are the oxidation reactions in solution, attributed to the NO_3^- ion in the presence of hydrogen ions. Such oxidation depends on the pH of the medium and the nature of the substance oxidized.

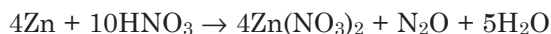
Nitric acid reacts with practically all common metals. Such reactions, however, can vary, forming different products depending on the position of the metal in electrochemical series, the concentration of nitric acid, temperature, and pH. Very weakly electropositive metals such as arsenic, antimony, or tin are oxidized to oxides in higher valence states; e.g.,



Metal oxides are formed as hydrates, like $\text{Sb}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. Nitric acid reacts with more electropositive metals forming nitrates and one of the oxides of nitrogen. The nature of NO_x formed depends on the position of the metal in the electrochemical series and temperature. Those metals that do not liberate hydrogen from dilute acids generally form nitric oxide and metal nitrates under cold or dilute conditions. While under warm or concentrated conditions of nitric acid, the same metals yield nitrogen dioxide and nitrates. An example is copper, which can generate nitric oxide or nitrogen dioxide from nitric acid. Its reaction with nitric acid under cold and warm conditions are shown below:

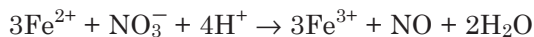


On the other hand, metals that are more electropositive than hydrogen, such as zinc and magnesium which liberate hydrogen from dilute acids, react with nitric acid to give nitrous oxide and the metal nitrates:



Magnesium may react with very dilute nitric acid liberating some hydrogen.

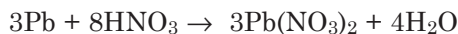
Nitric acid oxidizes most metal ions to their higher oxidation states:



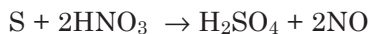
Concentrated nitric acid passivates many metals, such as, iron, cobalt, nickel, aluminum and chromium, forming a protective film of oxides on their surfaces, thus preventing any further reaction. Very dilute nitric acid is reduced by a strong reducing agents, such as metallic zinc, to form ammonia and hydroxylamine, NH_2OH .

Noble metals, such as gold, platinum, palladium, rhodium and iridium are not attacked by nitric acid at ordinary temperatures. These metals, however, dissolve in aqua regia (3:1 HCl — HNO_3 mixture). Nitric acid in aqua regia oxidizes gold to Au^{3+} , which readily combines with Cl^- to form soluble chloro-complex, AuCl_4^- .

Except silicon, all other carbon group metals, namely, germanium, tin, and lead, are oxidized by concentrated nitric acid. While germanium and tin form their dioxides, lead forms nitrate.



Concentrated nitric acid oxidizes nonmetals, such as sulfur, phosphorus, and iodine forming their oxyacids with liberation of nitric oxide. For example, cold concentrated nitric acid reacts with sulfur to form sulfuric acid:



Hot concentrated nitric acid reacts with iodine forming iodic acid:

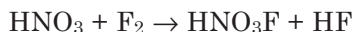


Similarly, phosphoric acid, H_3PO_4 , is obtained from reaction of nitric acid with violet phosphorus.

Among the oxygen group elements, while sulfur is oxidized to +6 oxidation state (in H_2SO_4), selenium and tellurium are oxidized to +4 oxyacids with the liberation of nitrogen dioxide:



Reaction with fluorine forms an unstable compound, 'fluorine nitrate', NO_3F :



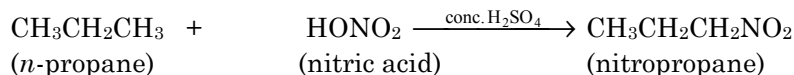
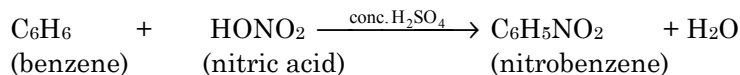
Nitric acid undergoes decomposition when heated above its boiling point or when exposed to light:

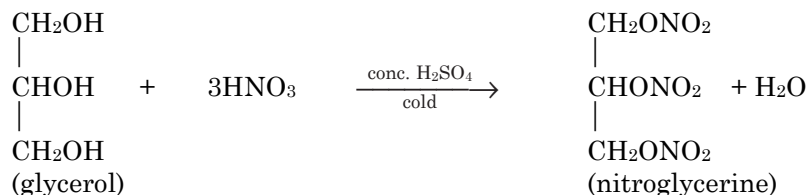


Nitric acid is used for nitration of many organic compounds. Many nitro derivatives are made by such reactions. Pure nitric acid or often its combination with concentrated sulfuric acid is employed in these syntheses. When pure nitric acid is dissolved in concentrated sulfuric acid, it forms nitronium ion, NO_2^+ , the active species in nitration reactions:

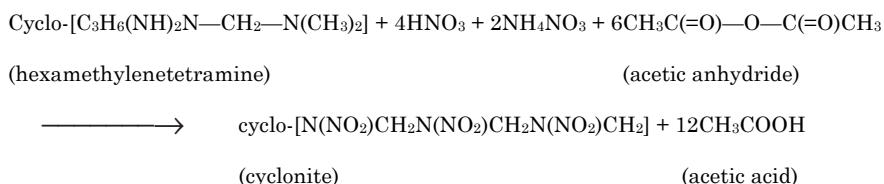


Nitration reactions are mostly substitution type, forming a wide variety of products including nitrobenzene, nitrotoluenes, nitroglycerine, nitrocellulose, trinitrotoluene, nitrophenols and nitroparaffins, many of which are known chemical explosives. Some examples are:





Cotton reacts with nitric acid to form a polymeric explosive material, nitrocellulose. Nitric acid reacts with hexamethylenetetramine, ammonium nitrate, and acetic anhydride to form cyclotrimethylenetrinitramine, a high explosive known as cyclonite, used to make plastic bombs:



Analysis

The strength of nitric acid can be determined by acid-base titration against a standard solution of a strong base such as NaOH using a color indicator, or by potentiometric titration using a pH meter. Nitrate ion, NO_3^- in its aqueous solution, may be measured with a nitrate ion-selective electrode or by ion chromatography following appropriate dilution.

Hazard

Because it is a strong oxidizing agent, nitric acid may undergo violent reactions with powerful reducing agents. Many nitration reactions of organics yield explosive products. Pure nitric acid is highly corrosive to skin causing severe injury. Concentrated acid (68.8 wt %) is moderately corrosive to skin. The acid may decompose under heating or photochemically, liberating toxic nitrogen dioxide gas.

NITRIC OXIDE

[10101-43-9]

Formula: NO; MW 30.006

Synonym: nitrogen monoxide

History, Occurrence, and Uses

Nitric oxide was discovered by Van Helmont in 1620. It occurs in the exhaust gases from automobiles along with other oxides of nitrogen, at trace concentrations. It also is found in minute quantities in the upper atmos-

phere, resulting from the oxidation of nitrogen in the presence of ionizing radiation or by electric discharge. Nitric oxide is the most stable oxide of nitrogen. It is used as an intermediate or as a starting reactant in the production of many nitrogen compounds, including nitrogen dioxide, nitric acid and nitrosyl chloride.

Physical Properties

Colorless gas; paramagnetic; density 1.3402 g/L; slightly heavier than air, air density 1.04 (air=1); liquefies at -151.8°C to a blue liquid; the refractive index of the liquid 1.330 at -90°C ; the density of the liquid 1.269 g/mL at -150.2°C ; solidifies at -163.6°C to a bluish-white snow-like solid; critical temperature -94°C ; critical pressure 65 atm; slightly soluble in water, 4.6 mL gas dissolves in 100 mL water at 20°C while 7.34 mL and 2.37 mL dissolve in the same volume of water at 0 and 60°C , respectively; more soluble in alcohol than water; soluble in carbon disulfide, and in ferrous sulfate solution (reacts).

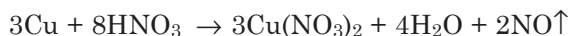
Thermochemical Properties

ΔH_f°	21.57 kcal/mol
ΔG_f°	20.69 kcal/mol
S°	50.35 cal/degree mol
C_p	7.13 cal/degree mol

Production

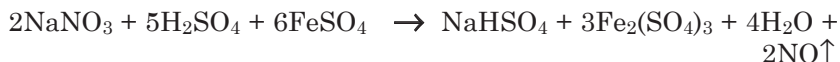
Nitric oxide is produced from nitrogen and oxygen by passing an electric spark through air or by bringing oxygen and nitrogen together at high temperatures. In either method, only small quantities of nitric oxide are generated.

Nitric oxide also can be made by reactions of nitric acid, nitrate, or nitrite salts with metals, metal oxides, or sulfates. Several metals react with nitric acid liberating nitric oxide. (See Nitric Acid, Reactions). For example, action of 1:1 nitric acid on copper turnings forms nitric oxide:



The above method does not yield pure nitric oxide.

In the laboratory pure nitric oxide may be prepared by warming a mixture of a nitrate salt with ferrous sulfate and concentrated sulfuric acid. The overall reaction may be written as:



Nitric acid formed as an intermediate by the action of sulfuric acid on nitrate is reduced by ferrous sulfate to produce nitric oxide. The reaction must be car-

ried out under only mild heating. Otherwise, under prolonged heating, nitric oxide may combine with any unreacted ferrous sulfate to form a brown ring derivative.

Another method of preparing pure nitric oxide is to heat nitrate-nitrite mixture with a metal oxide in a lower oxidation state:



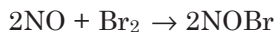
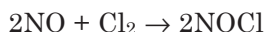
Reactions

Although nitric oxide is the most stable of all the oxides of nitrogen, it reacts spontaneously with oxygen forming nitrogen dioxide:



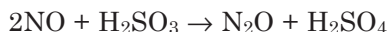
The above reaction is exothermic.

Reactions with chlorine and bromine form nitrosyl chloride and nitrosyl bromide, respectively:

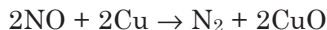


Nitric oxide readily loses an electron to form nitrosyl or nitrosonium ion, NO^+ , which is known to form salts, such as nitrosyl hydrogen sulfate, $(\text{NO})^+(\text{HSO}_4)^-$ or nitrosyl tetrafluoroborate, $(\text{NO})^+(\text{BF}_4)^-$.

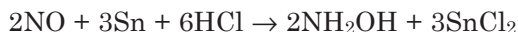
Nitric oxide is reduced to nitrous oxide by sulfurous acid:



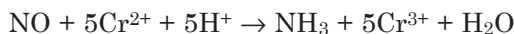
Also, it is reduced by several other reducing agents, forming a wide variety of products. For example, when nitric oxide is passed over a heated metal, such as copper or iron, it is reduced to nitrogen gas:



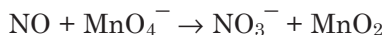
Tin, in the presence of hydrochloric acid, reduces nitric oxide to hydroxylamine. The overall molecular equation may be as follows:

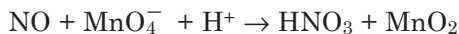


Chromium(II) salts in acid medium can reduce nitric oxide to ammonia:



Nitric oxide is oxidized to nitrate ion by permanganate ion. In acid medium, the products are nitric acid and manganese dioxide:





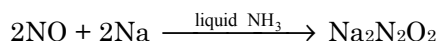
Nitric oxide forms a brown ring in cold ferrous sulfate solution (brown ring test for nitrates). The reaction involves the replacement of a water molecule by nitric oxide in hydrated ferrous ion:



A similar replacement reaction occurs with cyanide ion in the complex hexacyanoferrate(III):



Nitric oxide reacts with sodium in liquid ammonia forming sodium hyponitrite, an ionic compound of composition $\text{Na}_2^{2+}(\text{NO}^-)_2$:



Analysis

Nitric oxide is analyzed with GC using a TCD or by mass spectrometer using helium as a diluent and carrier gas. The characteristic mass for NO ion is 30. Also, it can be identified by the brown ring test in cold FeSO_4 solution (see Reactions). In contact with air it oxidizes to NO_2 , which is then identified from color, odor, and chemical properties.

Toxicity

Nitric oxide gas is moderately toxic. Exposure can cause severe irritation of the eyes, nose, and throat. Chronic inhalation produces pulmonary edema, irritation of the respiratory tract and corrosion of teeth.

NITROGEN

[7727-37-9]

Symbol: N; atomic number 7; atomic weight 14.0067; a Group V A (Group 15) nonmetallic element; occurs as diatomic gas; covalent molecule; Lewis structure :N≡N: ; bond length 1.10 Å; bond energy 226 kcal/mol; first ionization energy 335.4 kcal/mol; electronegativity 3.0; valence states -3, -2, -1, 0, +1, +2, +3, +4 and +5; more common valence states -3, +5, +4, +3, +2, +1; two stable isotopes, N-14 (99.63%) and N-15 (0.37%); six radioactive isotopes that have the mass numbers, 12, 13, 16, 17, 18, and 19; longest-lived radioisotope, N-13, $t_{1/2}$ 9.97 min.

History, Occurrence, and Uses

Nitrogen was discovered independently in 1772 by Swedish chemist Carl Scheele and Scottish botanist Daniel Rutherford. Priestly, Cavendish, and Lavoisier also obtained nitrogen independently more or less around the same time. Nitrogen was recognized first as an element by Lavoisier, who named it "azote", meaning "without life." The element was named nitrogen in 1790 by Chaptal. The name derived from the Greek name 'nitre' for potassium nitrate which contains nitrogen.

Nitrogen is the principal component of air. The earth's atmosphere constitutes about 78% nitrogen by volume. Nitrogen also occurs as nitrates in several minerals such as Chile saltpeter (sodium nitrate), niter or saltpeter (potassium nitrate) and minerals containing ammonium salts. Nitrogen is contained in many complex organic molecules including proteins and amino acids that occur in all living organisms. Nitrogen occurs ubiquitously all over the earth from the upper stratosphere and thermosphere to deep down in the crust from which it is outgassed continuously along with other deep earth gases. It is found in volcanic gases, mines, spring water, and absorbed in rocks. The concentration of nitrogen in the earth's crust is estimated to be 20 mg/kg. Its average concentration in seawater is about 0.5 mg/L. Nitrogen also is found in other planets. Its concentration in Mars' atmosphere is 2.6%.

Molecular nitrogen as a constituent of atmosphere serves as a diluent of oxygen in the air needed for breathing. Gaseous nitrogen has numerous uses in chemical, food, metal, and electrical industries. Nitrogen is needed in commercial production of ammonia (Haber process) and in preparation of many nitrides. It also is the starting material in making cyanamide salts, cyanides, and nitrogen oxides for producing nitric acid. Other applications are in gas chromatography, as a carrier gas, to provide an inert atmosphere in chemical reactions, to prevent oxidation reactions, to reduce fire or explosion hazards, and to dilute a reacting gas.

In the food industry nitrogen is used to prevent mold growth, spoilage from oxidation, and insect infestation.

Other miscellaneous applications of nitrogen gas include pressurizing cable jackets, preventing carburization in welding and soldering, inflating balloons, agitating liquid baths, and cooling catalytic reactors in petroleum refining.

Liquid nitrogen is used in rapid freezing of food and in its packaging, storage and transportation, for preserving blood, tissues, and bone marrow, for cryopulverizing plastics, resins, waxes, spices, and scrap rubber to achieve small particle size, and for deforming stainless steel to make high strength wires for springs.

Physical Properties

Colorless, odorless and tasteless gas; diamagnetic; density 1.229 g/L; converts to a colorless liquid at -195.79°C ; specific gravity of the liquid N_2 0.808; solidifies at -210°C ; solid nitrogen exists in two allotropic forms, a cubic alpha form and a hexagonal beta form; alpha allotrope changes to beta form at -237.5°C ; critical temperature -146.94°C ; critical pressure 33.46 atm; vapor pressure of the fluid at -203°C 5.1 torr; the gas is slightly soluble in water, 2.4

parts by volume dissolving in 100 parts water at 0°C; soluble in liquid ammonia; insoluble in alcohol.

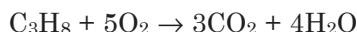
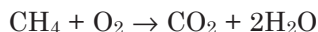
Thermochemical Properties

$\Delta H_f^\circ (\text{N}_2)$	0.0
$\Delta H_f^\circ (\text{N})$	112.78 kcal/mol
$\Delta G_f^\circ (\text{N}_2)$	0.0
$\Delta G_f^\circ (\text{N})$	108.89 kcal/mol
$S^\circ (\text{N}_2)$	45.77 cal/degree mol
$S^\circ (\text{N})$	36.61 cal/degree mol
$C_p (\text{N}_2)$	6.961 cal/degree mol
$C_p (\text{N})$	4.968 cal/degree mol

Production

All commercial processes involve either separation of nitrogen from air by cryogenic distillation or combustion of air with natural gas to remove oxygen. In the former process, air is liquefied and the liquid air is subjected to fractional distillation to separate its components.

In the combustion process, natural gas (methane), or propane or carbon is burned in air for the removal of oxygen:



The above reactions are exothermic and proceed to complete combustion. The gaseous mixture from combustion consists of nitrogen, carbon dioxide, water vapor and trace amounts of carbon monoxide and hydrogen. The mixture is cooled and the water vapor is condensed to liquid water, carbon dioxide and residual water is removed by adsorbing over molecular sieve.

Many nitrogen generator devices are commercially available to produce high purity gas in small amounts. In these, nitrogen is obtained from compressed air. It is separated from other air components by selective permeation through polymeric hollow fiber membranes after prefiltration.

In the laboratory, nitrogen may be generated by several methods, such as: thermal decomposition of ammonium dichromate:



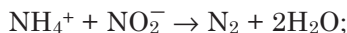
reaction of ammonia with bromine water:



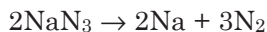
decomposition of ammonia with copper(II) oxide at elevated temperatures:



decomposition of ammonium nitrite in hot aqueous solution:



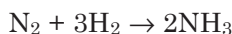
and carefully decomposing sodium azide:



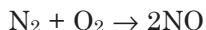
Reactions

At ordinary temperatures, nitrogen is very stable and chemically inert to most substances. However, at elevated temperatures and pressures or in the presence of an electric spark or ionization radiation, nitrogen can combine with many substances.

Nitrogen reacts with hydrogen at 400°C and 200 to 300 atm pressure in the presence of a catalyst, such as iron oxide, to form ammonia (the Haber process):



Nitrogen combines with oxygen at elevated temperatures, or when an electric spark is passed through its mixture with oxygen, nitrogen oxides are formed:



Ionization radiations also cause such combination, a process that occurs in the upper atmosphere forming oxides of nitrogen in low yields.

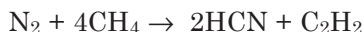
Nitrogen reacts with a mixture of red hot charcoal and sodium metal to form sodium cyanide:



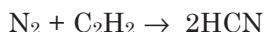
The cyanide salt also is obtained by heating nitrogen with a mixture of graphite and sodium carbonate at 900°C:



When nitrogen mixed with methane is passed through an electric arc, the products are hydrogen cyanide and acetylene:



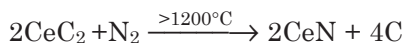
Nitrogen reacts with acetylene at 1,500°C forming hydrogen cyanide:



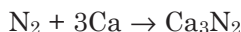
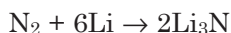
Nitrogen reacts with calcium carbide at high temperature to form calcium cyanamide:



Carbides of certain metals, such as cerium and uranium, react with nitrogen at very high temperatures forming their nitrides:



Nitrogen combines with alkali and alkaline earth elements at ordinary temperatures to form their nitrides:



However, its reactions with heavy metals at elevated temperatures form hard refractory interstitial nitrides of nonstoichiometric compositions.

Nitrogen at low pressure under electric discharge conditions produces a greenish-yellow glow, which continues to glow after the discharge. The molecular nitrogen is converted into active nitrogen that is chemically reactive and probably consists of excited nitrogen atoms and molecules at high energy levels. Such active nitrogen readily reacts with many unreactive elements in cold, such as mercury and sulfur, forming their nitrides.

Analysis

Nitrogen is analyzed by GC using a thermal conductivity detector and a molecular sieve, 5Å or equivalent column, and helium as the carrier gas. Its presence may be confirmed by mass spectrometry. The characteristic mass ion for GC/MS identification of N_2 is 28.

NITROGEN DIOXIDE

[10102-44-0]

Formula: NO_2 ; MW 46.0055; dimerizes to dinitrogen tetroxide, N_2O_4

Synonym: nitrogen peroxide

Occurrence and Uses

Nitrogen dioxide is an intermediate in producing nitric acid. It also is used in the lead chamber process for making sulfuric acid. It is used as a nitrating and oxidizing agent, in rocket fuels, in the manufacture of hemostatic cotton and other oxidized cellulose compounds, and in bleaching flour. Nitrogen dioxide occurs in trace concentrations in the atmosphere due to oxidation of nitric oxide in air. It also is found in exhaust gases of internal combustion engines, in industrial waste gases from plants using nitric acid, and in cigarette smoke. Brown color of smog in many industrial urban areas is attributed to nitrogen dioxide.

Physical Properties

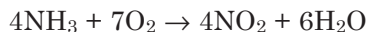
Reddish-brown gas; pungent irritating odor; liquefies to a yellow liquid at 21.2°C; liquefies under pressure to a brown fuming liquid, commercially known as nitrogen tetroxide which actually is an equilibrium mixture of nitrogen dioxide and dinitrogen tetroxide, N₂O₄; converts to a colorless crystalline solid at -11.2°C; refractive index 1.40 at 20°C; density of gas in air 1.58 (air=1); density of liquid 1.449 g/mL at 20°C; critical temperature 158.2°C; critical pressure 99.96 atm; decomposes in water forming nitric acid; reacts with alkalies; soluble in concentrated nitric and sulfuric acids; soluble in chloroform and carbon disulfide.

Thermochemical Properties

ΔH_f°	7.93 kcal/mol
ΔG_f°	12.26 kcal/mol
S°	57.35 cal/degree mol
C_p	8.89 cal/degree mol

Preparation

Nitrogen dioxide may be prepared by several methods. It is produced when an electric discharge is passed through air. It is made commercially from nitric oxide and air. Nitric oxide made by various processes (See Nitric Oxide) rapidly oxidizes to nitrogen dioxide. It is formed by decomposing nitric acid or by oxidizing ammonia with air:



Also, nitrogen dioxide can be made by heating copper with nitric acid.

In the laboratory, nitrogen dioxide is formed by heating lead nitrate or nitrate of another heavy metal:



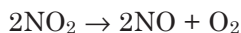
Gaseous mixture of nitrogen dioxide and oxygen is passed through a U-tube placed in a freezing mixture. Nitrogen dioxide condenses and is collected as liquid.

Reactions

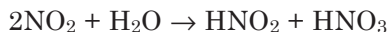
The oxidation state of nitrogen in nitrogen dioxide is +4. The molecule has an unpaired electron. Both these factors contribute to its reactivity.

Nitrogen dioxide readily converts to other forms of nitrogen oxides. It coexists in equilibrium with its dimeric form, N₂O₄. The latter is more stable at ordinary temperatures.

When heated above 150°C, nitrogen dioxide dissociates to nitric oxide and oxygen:



Nitrogen dioxide dissolves in cold water, forming a mixture of nitrous acid and nitric acid:



Nitrous acid readily decomposes to nitric acid and nitric oxide:

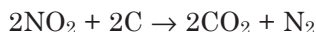
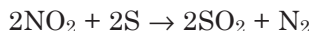


The overall reaction is as follows:

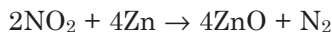
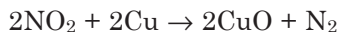


When dissolved in warm water, no nitrous acid forms.

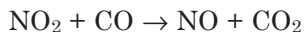
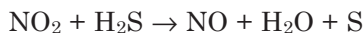
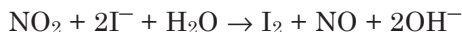
Nitrogen dioxide is a strong oxidizing agent. It oxidizes both nonmetals and metals, forming their oxides and itself reduced to nitrogen. Thus, sulfur, phosphorus and charcoal burn in nitrogen dioxide to yield oxides of these elements and nitrogen:



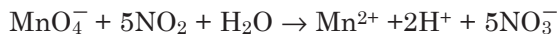
Copper, zinc, iron and many other metals are similarly converted to their oxides when heated with nitrogen dioxide:



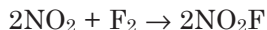
Nitrogen dioxide oxidizes an aqueous solution of iodide to iodine, hydrogen sulfide to sulfur, and carbon monoxide to carbon dioxide. In such reaction, it is reduced to nitric oxide, rather than nitrogen:



With stronger oxidizing agents, nitrogen dioxide acts as a reducing agent. Thus, it reduces permanganate, MnO_4^- , to Mn^{2+} ion, decolorizing its solution. In this reaction, it is oxidized to nitrate ion:



Reaction with fluorine forms nitryl fluoride, NO_2F :



Nitrogen dioxide reacts with alkalis, giving a mixture of nitrite and nitrate:



Analysis

Nitrogen dioxide can be identified by color, odor, and physical properties. It is dissolved in warm water and converted to nitric acid. The latter may be measured by acid-base titration or from analysis of nitrate ion by nitrate ion-specific electrode or by ion chromatography. Alternatively, nitrogen dioxide may be passed over heated charcoal to produce nitrogen and carbon dioxide that may be analysed by GC-TCD or GC/MS (See Nitrogen, Analysis). The characteristic masses for N_2 and CO_2 formed for their identification are 28 and 44, respectively.

Hazard

Nitrogen dioxide is highly toxic. Exposure can cause strong irritation of the nose, throat, and respiratory tract. The toxic symptoms include cough, frothy sputum, chest pain, difficulty in breathing, and cyanosis with delayed effects—that may progress to hemorrhage, lung injury, and death (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons). Being a strong oxidant, its reactions with many oxidizable substances may proceed to explosive violence.

NITROGEN PENTOXIDE

[10102-03-1]

Formula: N_2O_5 ; MW 108.01

Synonyms: dinitrogen pentoxide; nitric anhydride; nitric acid anhydride.

Uses

Nitrogen pentoxide dissolved in chloroform is used as a nitrating agent in organic synthesis.

Physical Properties

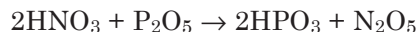
Colorless hexagonal crystal; volatile solid; density 1.642 g/cm^3 at 18°C; melts at 30°C; decomposes at 47°C; soluble in water forming nitric acid; soluble in chloroform with some decomposition.

Thermochemical Properties

ΔH_f° (cry)	-10.31 kcal/mol
ΔH_f° (gas)	2.70 kcal/mol
ΔG_f° (cry)	27.2 kcal/mol
ΔG_f° (gas)	27.5 kcal/mol
S° (cry)	42.6 cal/degree mol
S° (gas)	85.0 cal/degree mol
C_p (cry)	34.2 cal/degree mol
C_p (gas)	20.2 cal/degree mol

Preparation

Nitrogen pentoxide is obtained by dehydration of pure nitric acid by phosphorus(V) oxide at low temperatures around -10°C :

**Reactions**

Nitrogen pentoxide is an anhydride of nitric acid. It dissolves in water to form nitric acid:



Its reactions in aqueous medium are those of nitric acid.

Nitrogen pentoxide is an unstable compound. Its vapors decompose to nitrogen dioxide and oxygen when heated at 45°C :

**Analysis**

Nitrogen pentoxide may be dissolved in water and the aqueous solution analyzed for nitric acid by acid-base titration or potentiometric titration. Alternatively, the oxide is dissolved in chloroform, diluted appropriately, and analyzed by GC/MS using a polar GC column.

Toxicity

Nitrogen pentoxide is toxic by ingestion and can produce mouth burn. Skin contact can cause irritation.

NITROGEN TETROXIDE

[10544-72-6]

Formula: N_2O_4 ; MW 92.011; a dimer of nitrogen dioxide, NO_2 ; exists in equilibrium with NO_2

Synonym: dinitrogen tetroxide

Uses

Nitrogen tetroxide is a solvent and a powerful and selective oxidizing agent. Its adducts with organic solvents are used to synthesize nitrates of noble metals.

Physical Properties

Colorless liquid or gas; exists in equilibrium with NO_2 ; density 1.45 g/mL at 20°C; boils at 21.25°C; freezes at -9.35°C to a colorless diamagnetic solid; critical temperature 157.85°C; critical pressure 99.64 atm; critical volume 167 cm³/mol; reacts with water.

Thermochemical Properties

ΔH_f° (liq)	-4.66 kcal/mol
ΔH_f° (gas)	2.20 kcal/mol
ΔG_f° (liq)	23.30 kcal/mol
ΔG_f° (gas)	23.40 kcal/mol
S° (liq)	50.0 cal/degree mol
S° (gas)	72.73 cal/degree mol
C_p (liq)	34.11 cal/degree mol
C_p (gas)	18.48 cal/degree mol
ΔH_{vap}	9.11 kcal/mol
ΔH_{fus}	3.50 kcal/mol
ΔH_{diss} (gas)	13.6 kcal/mol

Preparation

Nitrogen tetroxide always is formed along with nitrogen dioxide during preparation of the dioxide (See Nitrogen Dioxide.) Mixed oxides are produced by oxidation of nitric oxide (NO) in air, heating metal nitrates, or by metals reacting with nitric acids or nitrates.

Reactions

The tetroxide occurs along with the dioxide, NO_2 , in an equilibrium that is highly dependent on temperature.



While low temperature favors dimeric tetroxide, equilibrium shifts toward dioxide at higher temperatures. Thus, at 100°C the composition of the vapor is 90% NO_2 and 10% N_2O_4 . At 140°C, the tetroxide completely dissociates into dioxide. At 150°C, thermal dissociation of dioxide begins, giving NO and O_2 . Decomposition of NO_2 is complete at about 600°C. At 21.15°C, the boiling point of N_2O_4 , the liquid composition is 99.9% N_2O_4 and 0.1% NO_2 .

Reactions of N_2O_4 are the same as those involving NO_2 (See Nitrogen Dioxide, Reactions.) The tetroxide is a strong oxidizing agent in aqueous solution.

Nitrogen tetroxide readily forms adducts with many organic compounds including aromatics, and heterocyclic compounds of nitrogen and oxygen, such

as pyridine (py) and tetrahydrofuran (THF), respectively. Examples are $\text{N}_2\text{O}_4 \cdot \text{py}$ and $\text{N}_2\text{O}_4 \cdot \text{THF}$.

Many metals, such as Cu, Zn, and Fe dissolve in a mixture of N_2O_4 and organic solvent forming their nitrate— N_2O_4 adducts. Nitrate adducts with N_2O_4 having compositions: $\text{Cu}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_4$, $\text{Fe}(\text{NO}_3)_2 \cdot 1.5\text{N}_2\text{O}_4$, and $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$ are known. (Cotton, F. A., Wilkinson, G., Murillo, C.A. and M. Bochmann. 1999. *Advanced Inorganic Chemistry*, 6th ed. pp 329-30. New York: John Wiley & Sons.)

Nitrogen tetroxide dissociates completely in anhydrous nitric acid forming NO^+ and NO_3^- ions:



Nitrogen tetroxide reacts with concentrated sulfuric acid forming NOHSO_4 along with nitric acid and sulfur trioxide. A simplified balanced reaction may be written as follows:



Analysis

Nitrogen tetroxide may be identified from physical and chemical properties and its ready conversion to NO_2 gas which may be identified by its brown red color, pungent odor, and chemical analysis (See Nitrogen Dioxide, Analysis.)

Hazard

See Nitrogen Dioxide, Hazard.

NITROGEN TRICHLORIDE

[10025-85-1]

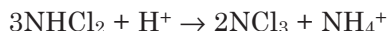
Formula: NCl_3 ; MW 120.365

Synonyms: nitrogen chloride; chlorine nitride; trichlorine nitride

Uses

Nitrogen trichloride bleaches and sterilizes flour. It also preserves citrus fruits.

Nitrogen trichloride may be found in treated wastewater due to chlorine added as a bactericide reacting with dissolved ammonia. Such reactions may form monchloro- and dichloramine, and nitrogen trichloride:



Physical Properties

Yellow, oily, heavy liquid; pungent odor; density 1.653 g/mL; freezes to rhombohedral crystalline solid below -40°C ; evaporates in air rapidly; vapor

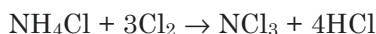
pressure 150 torr at 20°C; explodes when heated at 93°C; highly unstable, decomposes explosively in light; insoluble in water, decomposes slowly in cold water after several hours; decomposes in hot water; soluble in benzene, chloroform, carbon tetrachloride, carbon disulfide and phosphorus trichloride.

Thermochemical Properties

$$\Delta H_f^\circ (\text{liq}) \quad 54.97 \text{ kcal/mol}$$

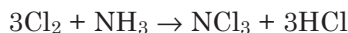
Preparation

Nitrogen trichloride is prepared by passing chlorine gas into slightly acid solution of ammonium chloride. The product is continuously extracted with carbon tetrachloride:



Hypochlorous acid, HOCl, also may be used instead of chlorine in such preparation.

Nitrogen trichloride can be prepared by the action of anhydrous chlorine with anhydrous ammonia:



Nitrogen trichloride is made commercially by electrolyzing an acidified solution of ammonium chloride.

Hazard

Nitrogen trichloride is an explosive compound. It explodes when heated at 93°C or when exposed to sunlight. Also, explosive reactions occur with ozone and many organic substances.

NITROGEN TRIFLUORIDE

[7783-54-2]

Formula: NF_3 ; MW 71.002

Synonym: nitrogen fluoride

Physical Properties

Colorless gas; moldy odor; liquefies at -128.75°C ; density of liquid 3.116 g/mL; vapor pressure at -158°C 96 torr; solidifies at -206.8°C ; critical temperature -39.15°C ; critical pressure 44.02 atm; critical volume 126 cm^3/mol ; very slightly soluble in water.

Thermochemical Properties

$$\begin{array}{ll} \Delta H_f^\circ & -31.57 \text{ kcal/mol} \\ \Delta G_f^\circ & -21.66 \text{ kcal/mol} \\ S^\circ & 66.33 \text{ cal/degree mol} \end{array}$$

C_p
 ΔH_{vap}

12.76 cal/degree mol
 2.76 kcal/mol

Preparation

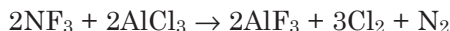
Nitrogen trifluoride is prepared by electrolysis of either molten ammonium fluoride, NH_4F , or melted ammonium acid fluoride, NH_4HF_2 (or ammonium fluoride in anhydrous HF). While the NH_4F method is preferred because it forms nitrogen trifluoride as the only product, electrolysis of ammonium acid fluoride yields a small amount of dinitrogen difluoride, N_2F_2 , and NF_3 .

Also, nitrogen trifluoride can be prepared by reaction of ammonia with fluorine diluted with nitrogen in a reactor packed with copper. Other nitrogen fluorides, such as N_2F_2 , N_2F_4 , and NHF_2 also are produced. The yield of major product depends on fluorine/ammonia ratio and other conditions.

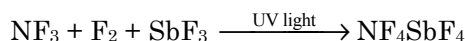
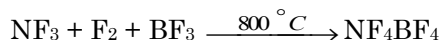
Reactions

Nitrogen trifluoride is very stable at ambient temperatures. It is much less reactive than other nitrogen trihalides. The molecule has a very low dipole moment and the lone pair of electrons on the nitrogen atom does not usually form complexes.

Nitrogen trifluoride reacts with aluminum chloride at 70°C forming N_2 , Cl_2 and AlF_3 :

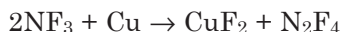


Nitrogen trifluoride also reacts with fluorine and strong Lewis acids, such as BF_3 , AsF_5 and SbF_5 under pressure. Reactions occur at low temperatures and in the presence of UV radiation to form tetrafluoroammonium salts:



Tetrafluoroammonium salts hydrolyze in water, regenerating NF_3 .

Nitrogen trifluoride reacts with several metals at high temperatures. When heated with copper, it yields copper(II) fluoride and dinitrogen tetrafluoride:



Heating with powdered titanium, zirconium, tin, and other metals at 250°C produces fluorides.

Reactions with reducing agents such as H_2 , H_2S , NH_3 , CO , carbon, and diborane, especially under pressure and high temperatures, can be violent.

Toxicity

Nitrogen trifluoride is mildly toxic. Prolonged exposure can cause mottling of teeth and skeletal changes. LC_{50} inhalation (mouse): 2,000 ppm/4hr.